Polymerization of Methacrylates in twin screw extruders

Jongbloed, Hetty Aletta

8. Summary and conclusions

As an alternative for conventional polymerization processes which often require the use of solvents, the possibilities of two types of extruder as polymerization reactors for methacrylates were investigated. Experiments were performed in both a closely intermeshing counterrotating twin screw extruder and a selfwiping corotating twin screw extruder. These extruders differ not only in the direction of the screw rotation, but also in the geometry of the screws.

8.1 Kinetic investigations

To investigate the differences in operability between the two extruders, two polymerizations were used, namely the homopolymerization of n-butylmethacrylate (BMA) and the copolymerization of BMA with 2-hydroxypropylmethacrylate (HPMA). Both reactions are free radical addition polymerizations. The homopolymerization of BMA was described in an earlier study [1]. In this thesis kinetic investigations concerning the copolymerization of BMA with HPMA were performed.
The reactivity ratios of the copolymerization (equation 3.5) were found to be:

$$r_1 = 1.04$$
$$r_2 = 0.92$$

These values imply that no shift in the copolymer composition occurs during the polymerization.
The polymerization enthalpy of the copolymerization was obtained using Differential Scanning Calorimetry (DSC). This resulted in:

$$\Delta H_p = 60.0 \pm 0.5 \text{ kJ/mol}$$

The course of the copolymerization obtained with DSC experiments was compared to the course of the two individual homopolymerizations of BMA and HPMA. The most important differences between these reactions were the reaction velocity, i.e. the time needed to attain a certain required conversion, and the enhancement of the reactions

due to the viscosity of the reacting medium. The copolymerization of BMA with HPMA proceeds faster and has a more viscous product than the homopolymerization of BMA.

8.2 Reactive extrusion results

8.2.1 Counterrotating extruder

An investigation of the reactive extrusion process in a counterrotating extruder was carried out with the copolymerization of BMA with HPMA. The effect of reaction and extrusion parameters like the throughput, the barrel temperature, the die resistance and the screw rotation rate on the product was analysed. Conversions up to 93% were obtained and the weight average molecular weight ranged between 31 and 86 kg/mol. Although no major problems were encountered in the process, it appeared that the course of the polymerization and the properties of the product are strongly dependent on the adjustment of the aforementioned parameters. The influence of these parameters on the product originates from their influence on the residence time in the extruder and the temperature of the material in the extruder. Both residence time and material temperature are crucial aspects in a reactive extrusion process, because both aspects determine the degree to which the reaction can take place. For example, an increase of the throughput resulted in a decrease of the residence time and thereby in a decrease in conversion. At the same time more heat is generated within the extruder if the throughput is increased, which resulted in a decrease of the average molecular weight.
In short, every parameter adjustment may lead to a different product quality.

8.2.2 Selfwiping extruder

Both the homopolymerization of BMA and the copolymerization of BMA with HPMA were studied in a selfwiping extruder. Conversions up to 95% were obtained with both reactions and the weight average molecular weight ranged from 37 to 67 kg/mol for BMA and from 20 to 85 kg/mol for BMA-co-HPMA. However, the two reactions showed remarkable differences in operability limitations in the extruder. When the polymerization of BMA was performed, instabilities consisting of a variable discharge rate could occur. These instabilities are the result of the transport mechanism in the selfwiping extruder: the drag flow in this type of extruder is dependent on the rheology of the material. In order to transport the material by drag a certain viscosity is required. To investigate the flow mechanism in the selfwiping extruder experiments were

performed in a perspex model. It was observed that in the partially filled zone of an extruder a low viscosity material (η<1 Pa·s) was transported by the pushing action or the displacement action of the screws and not by drag. Only materials with a relatively high viscosity (estimated about 10 Pa·s and higher) can be transported by pure drag. The foregoing has enormous consequences for the fluid distribution in the extruder. As a result, the hold-up and thereby the residence time in the extruder is influenced by the viscosity of the material. The copolymerization of BMA with HPMA could be performed successfully for every adjustment of the extrusion parameters used, due to the higher reaction velocity and higher viscosity compared to BMA.
Just like in the counterrotating extruder, the influence of the reaction and extrusion parameters on the product quality is based on the influence of these parameters on the residence time and the material temperature.
In addition to the model experiments concerning the flow in a selfwiping extruder, the residence time distribution (RTD) in the selfwiping extruder was measured. This was done for non-reacting materials as well as for the copolymerization of BMA with HPMA. It was observed that the RTD of the polymerizing system showed a much wider spread than the non-reacting system, independent of the hold-up in the extruder. This can be attributed to the large viscosity increase from feed end to die which leads to a combination of transport mechanisms and results in a good axial mixing.

8.3 General conclusions

The results described in this thesis show that both a counterrotating and a selfwiping extruder can be used as a reactor for the bulk polymerization of methacrylates. By adjusting the extrusion parameters the process and the product quality can be controlled. However, for a successful reactive extrusion process the reaction velocity must be high enough to attain the required degree of conversion in the limited residence time within the extruder.
Although both types of extruder which were used could be operated successfully, an important difference in operability limitations was observed between the two extruders. When a relatively slow polymerization was carried out in the selfwiping extruder, the throughput could not be increased as much as in the counterrotating extruder without endangering the stability of the process. This was due to the differences in transport mechanism between the two extruders. For slow polymerizations the use of a counterrotating extruder is preferred to a selfwiping extruder. For fast reactions higher output rates can be obtained with the selfwiping extruder, due to its higher pump capacity.

In an attempt to generalize the results as a basis for scale-up, it was concluded that the most important aspect for scale-up is the heat production of the reaction. An increase of the screw diameter involves a relative decrease of the heat transfer, so the material temperature increases. Because this may lead to unfavourable results, the straightforward scale-up of a reactive extrusion process is limited. However, in order to limit the temperature increase which is inherent in scale-up, other possibilities exist besides decreasing the barrel temperature. For certain products a prepolymerization of the monomer outside the extruder can be a solution. In this way the heat production in the extruder is limited and the viscosity and the material transport are enhanced. Other options are, for example, the incorporation of a cold side feed in the extrusion process or the degassing of an inert volatile material.

8.4 Reference

1. K.J. Ganzeveld and L.P.B.M. Janssen, *Can. J. Chem. Eng.*, **71**, 411 (1993).